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Group velocity delay spectroscopy technique for industrial monitoring of electron beam induced vapors

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ABSTRACT

Spectroscopic techniques are ideal for characterization and process control of electron beam generated vapor plumes. Absorption based techniques work well for a wide variety of applications, but are difficult to apply to optically dense or opaque vapor plumes. We describe an approach for monitoring optically dense vapor plumes that is based on measuring the group velocity delay of a laser beam near an optical transition to determine the vapor density. This technique has a larger dynamic range than absorption spectroscopy. We describe our progress towards a robust system to monitor aluminum vaporization in an industrial environment. Aluminum was chosen because of its prevalence in high performance aircraft alloys. In these applications, composition control of the alloy constituents is critical to the deposition process. Data is presented demonstrating the superior dynamic range of the measurement. In addition, preliminary data demonstrating aluminum vapor rate control in an electron beam evaporator is presented. Alternative applications where this technique could be useful are discussed.

Keywords: Group velocity delay spectroscopy, optical beat signal, optical heterodyne, index of refraction, laser absorption spectroscopy, external cavity diode laser (ECDL), electron beam vaporization, vapor density, vapor phase manufacturing, process control

1. INTRODUCTION

Electron beam physical vapor deposition (EB-PVD) is the method of choice for high rate deposition processes.[1] These processes are especially challenging for process monitoring. Standard vapor process monitors (quartz crystal microbalances, ionization type monitors) are invasive and have short lifetimes in high vapor flux environments. Spectroscopic techniques offer an ideal approach for monitoring the pertinent characteristics of electron beam produced vapor plumes. In particular, laser absorption spectroscopy (LAS) continues to be a useful tool for accurately measuring the absolute vapor composition a variety of physical vapor deposition processes. LLNL has demonstrated such systems for the vaporization titanium alloys,[2] a uranium-iron alloy,[3] and is now developing a similar system for monitoring the evaporation of zirconium oxide for the production of thermal barrier coatings.

A key component in any absorption spectroscopy based density monitoring system is the light source. Presently, the majority of laser systems used for spectroscopy are based on argon-ion ring dye lasers. Ring dye laser systems are very flexible in terms of tunability and output power, but their cost, size, and maintainability make them impractical for most industrial settings. The feasible transfer of LAS technology from a laboratory setting to an industrial environment requires the replacement of the argon-ion pumped ring dye laser by a laser diode. The diode laser must be compact, single longitudinal mode, and scannable. Single mode tunable external cavity diode lasers (ECDLs) are now commercially available at various wavelengths throughout the IR. Their narrow linewidth, tunability, compact size, and low power requirements, make the ECDL an appropriate choice for laser absorption spectroscopy applications in industrial settings.

The ease of implementation and the broad experience base have made laser absorption spectroscopy straightforward to implement for certain applications. But, laser absorption spectroscopy (LAS) is only well-suited to monitoring the density of vapors where the absorption is limited to the range of 10-90%. This is the equivalent to a factor of about 22 in density (≈13 dB dynamic range). This limit in the dynamic range requires that each process must be matched to an unique optical transition that falls within the acceptable limits for minimum and maximum absorption (10% - 90%). Since the amount of absorption is determined by both the process of interest and the specific process geometry, process monitoring using laser absorption spectroscopy must be tailored to each installation. Therefore it is unlikely that LAS will see broad commercial acceptance or application for process control.

An alternate method we are pursuing is based on measuring the laser group velocity delay near an optical transition to determine the vapor density. The dynamic range of vapor density measurements performed using group velocity delay spectroscopy (GVDS) is much higher (30 dB and greater) than the dynamic range of LAS. In fact, the GVDS density measurement method can resolve the density of vapor plumes that are completely opaque at line resonance. Both LAS and GVDS density measurement methods will be explained and compared. It will be shown that while both methods have a place in the industrial process control of EB-PVD applications, the group velocity delay (GVDS) method shows promise as a more widely adaptable EB-PVD process control sensor.

2. ELECTRON BEAM PHYSICAL VAPOR DEPOSITION (EB-PVD)

Electron beam physical vapor deposition (EB-PVD) is a well established method for high-rate vapor deposition. The manufacture of metal matrix composites,[2] optical coatings,[9, 10] and oxide coatings on turbine blades[8] all use EB-PVD to produce high quality economical coatings. Electron beam vaporization has the advantage of high deposition rates, low contaminant introduction, and good microstructure control. Figure 1 shows a schematic of an electron beam evaporator. Electrons leaving the electron gun are electro-magnetically guided to the hearth. Most of the electron beam energy is deposited into the material contained in the hearth, resulting in the vaporization of the target material. The vapor is then collected on the part at some distance above the melt. This approach works well for alloys whose constituents have vapor pressures within a factor of approximately 100. When the constituent vapor pressures are close to each other, steady-state vaporization with the proper vapor composition can be achieved. However, when the vapor pressures of the alloy constituents differ by significantly larger factors, the vapor composition varies as the higher vapor pressure constituent are depleted from the hearth. Active correction for these fluctuations is possible if the vapor composition is known.

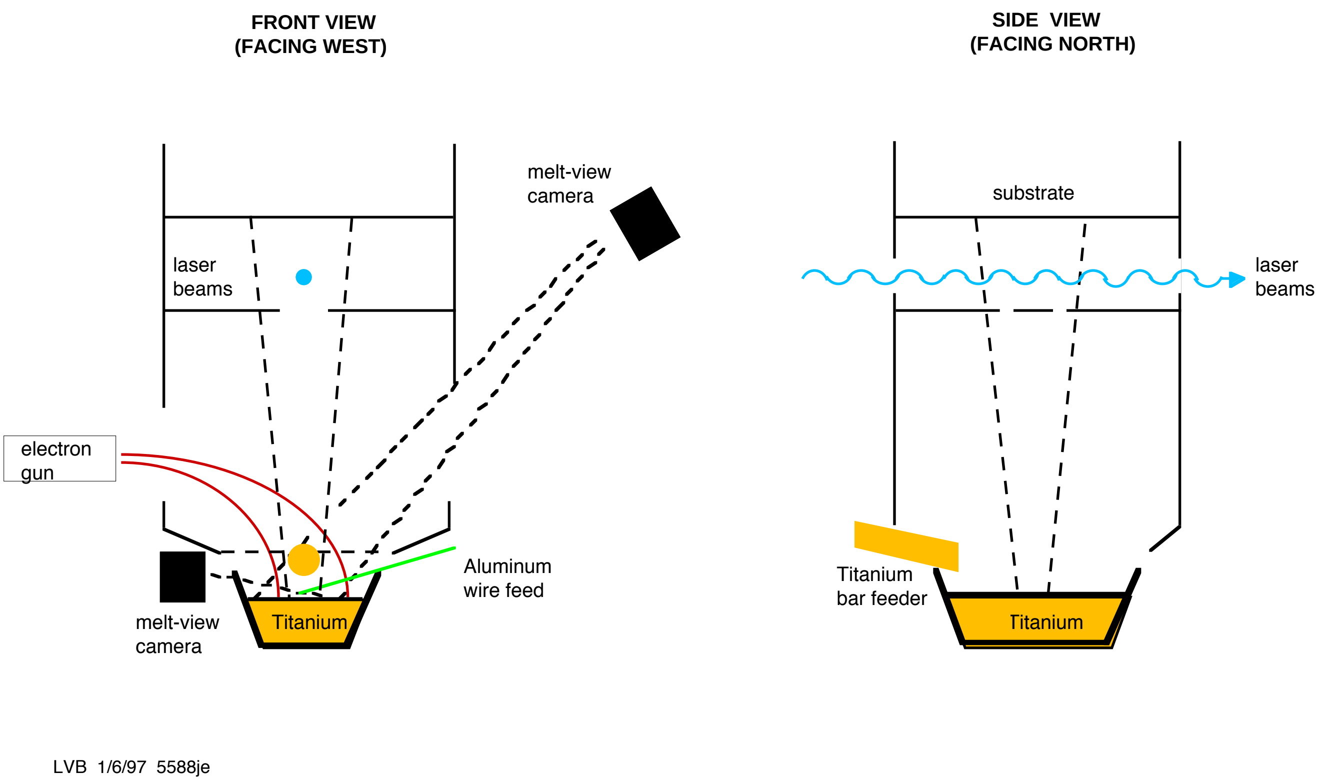

Figure 1.

Schematic of an electron beam evaporator

A good example of difficult alloys to deposit congruently are titanium-aluminum alloys. These alloys are of particular interest for use in aircraft engine components because of their high temperature material properties. But at typical vaporization temperatures, the vapor pressures of titanium and aluminum differ by a factor of approximately 200. This difference can lead to unacceptable variations in the composition of the deposited film. Several techniques have been used to minimize these variations with various degrees of success. Enriching the feedstock with the more volatile components has had some success in producing more stoichiometric Ti-6Al-4V films. This approach is relatively costly in that special feedstock must be procured. In bottom fed systems, controlling the melt level has had limited success in producing uniform films. Also, variations in the feed rate caused by stiction produce fluctuations in the films composition. Figure 2 shows an example of titanium/aluminum vapor rate data. The titanium vapor was monitored by a LAS sensor while the aluminum vapor was monitored by a GVDS sensor. The titanium vapor rate was controlled by means of keeping the melt pool height at a constant level. The aluminum vapor rate, however, varies widely even with the melt height held approximately constant. This illuminates the need for a vapor rate control method for optically dense vapors such as aluminum.

Clearly, a more direct measure of the what is being deposited would be useful for controlling the vaporization process.   In the following sections we discuss two spectroscopic techniques we have used to monitor and control electron beam vaporizers.

(graph of Ti vapor control goes here)

Time

Figure 2.

Titanium and aluminum density signals for the co-evaporation of Ti-(22 wt%) Al. In this experiment pool height was used as a control parameter.

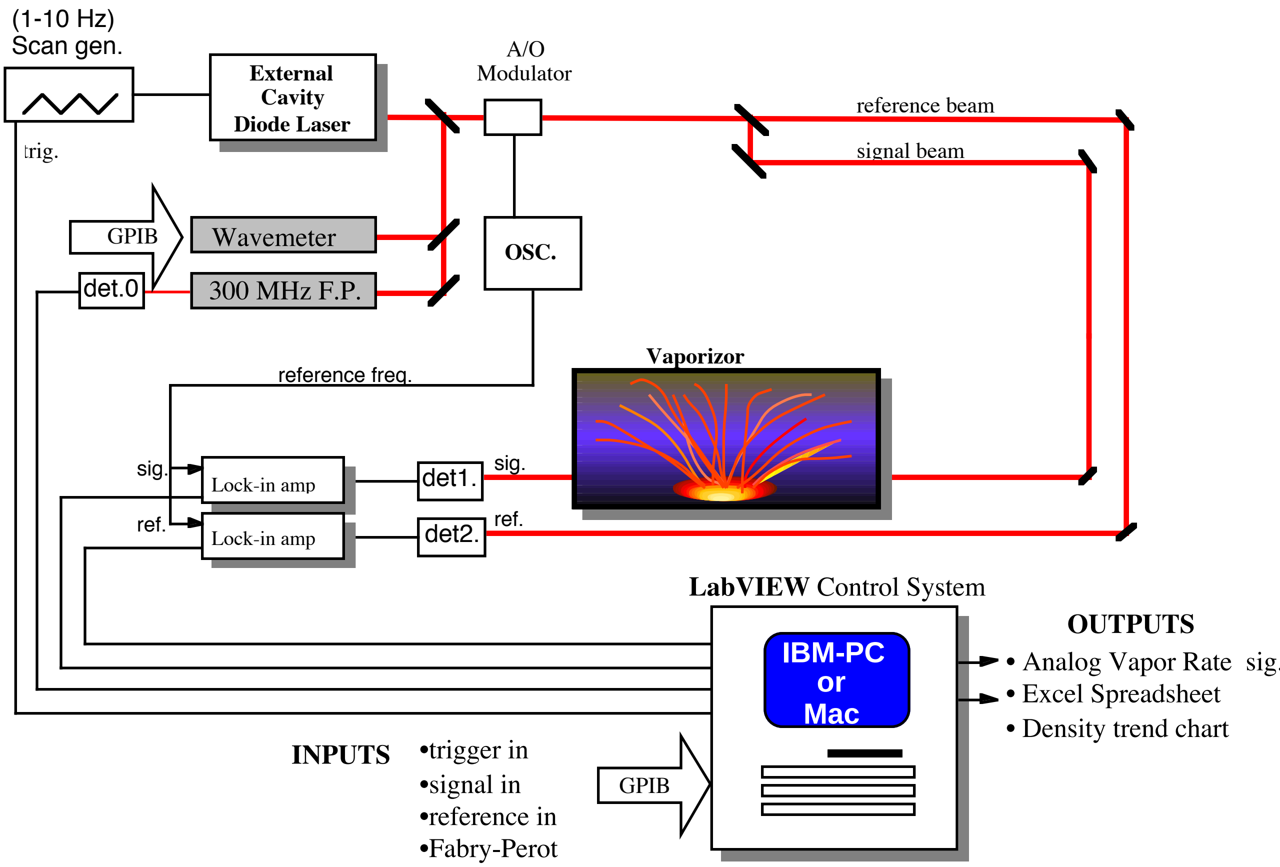

Figure 3.

Laser Absorption Spectroscopy (LAS) Vapor Density Monitor

3. ABSORPTION SPECTROSCOPY DESCRIPTION AND SIGNAL ANALYSIS

Laser absorption spectroscopy has been used to monitor electron beam generated vapor plumes at Lawrence Livermore National Laboratory for more than twenty years. LAS has proven itself to be an accurate and reliable means to monitor both density and composition. During this time, the diagnostic has moved from a research tool to being a robust component in a process control system.

In LAS, the laser light absorbed by the vapor is a measure of the vapor density. By scanning the laser wavelength slightly wider than the atomic transition, a zero baseline is established, thus providing an absolute calibration for each scan. LAS is also very attractive for composition monitoring and control as it is highly selective. Interference from other elements is very unlikely due to the narrow laser linewidth, as well as to the large separation of atomic transitions as compared to the transition linewidth.

Figure 3 illustrates the key components in an industrial LAS density monitoring system. As mentioned previously, the laser diode makes the system compact, reliable and economical. The Acousto-Optic (A/O) modulator and lock-in-amplifier (LIA) combination allow for synchronous detection for improved signal-to-noise, as well as the ability to monitor multiple species simultaneously. Synchronous detection is especially critical for monitoring electron beam vaporizer systems as the background light incident on the detector is more than an order of magnitude higher power than the typical laser powers. A reference detector located just prior to the vessel entrance provides a means to ratio out any laser amplitude or light delivery fluctuations which would have been interpreted as density fluctuations. The computer takes the outputs of the signal and reference LIAs and calculates state density using an algorithm based on Beer's Law,

$$T = e^{-\eta\sigma\ell} \qquad (1)$$

$$\begin{aligned} &where \\ &T = Transmission \\ &\eta = state\ density \\ &\sigma = the\ cross\ \sec tion\ of\ the\ atomic\ transition \\ &\ell = pathlength \end{aligned}$$

$$\eta = -\int \frac{\ln(T)}{\sigma\ell} \qquad (2)$$

Figure 4 shows a typical titanium vapor absorption scan. By re-arranging equation 1, the state density can be calculated. Integration of the waveform in frequency space yields the state density. The total density is then calculated based on an assumed (or measured) electronic temperature. The total density can either be passed directly to the control system or can first be converted to a vaporization rate with the use of a model. The vaporizer control system uses the total density or vaporization rate to adjust parameters such as feed rate and electron beam current to maintain the desired setpoint.[2]

Once an atomic transition is identified that matches the process and available laser technology,[4] deploying a LAS diagnostic is straightforward. The remaining components are standard optical and opto-electronic components. Some care must be taken to eliminate optical power variations due to etalons and polarization effects. But once properly deployed, a LAS diagnostic provides a robust vapor monitoring system. With the advent of relatively inexpensive and simple to operate external cavity diode laser (ECDL) systems, LAS will continue to be seen in vapor phase manufacturing process control applications.

4. GROUP VELOCITY DELAY SPECTROSCOPY DESCRIPTION AND SIGNAL ANALYSIS

Group velocity delay spectroscopy relies on the wavelength dependent phase delay induced by the vapor plume near an atomic transition to monitor the transition density. A frequency dependent index of refraction in a vapor plume is a characteristic of an atomic transition. Several techniques take advantage of this behavior including the hook method and the related fringe-shift method.[5] The group velocity delay technique is essentially the frequency analog of the hook method. Whereas the hook method works in wavelength space and uses an interferometer to generate the phase difference, the group velocity delay technique uses a beat signal to transform the technique into the frequency regime and can use fast photodiodes to determine the phase shift.

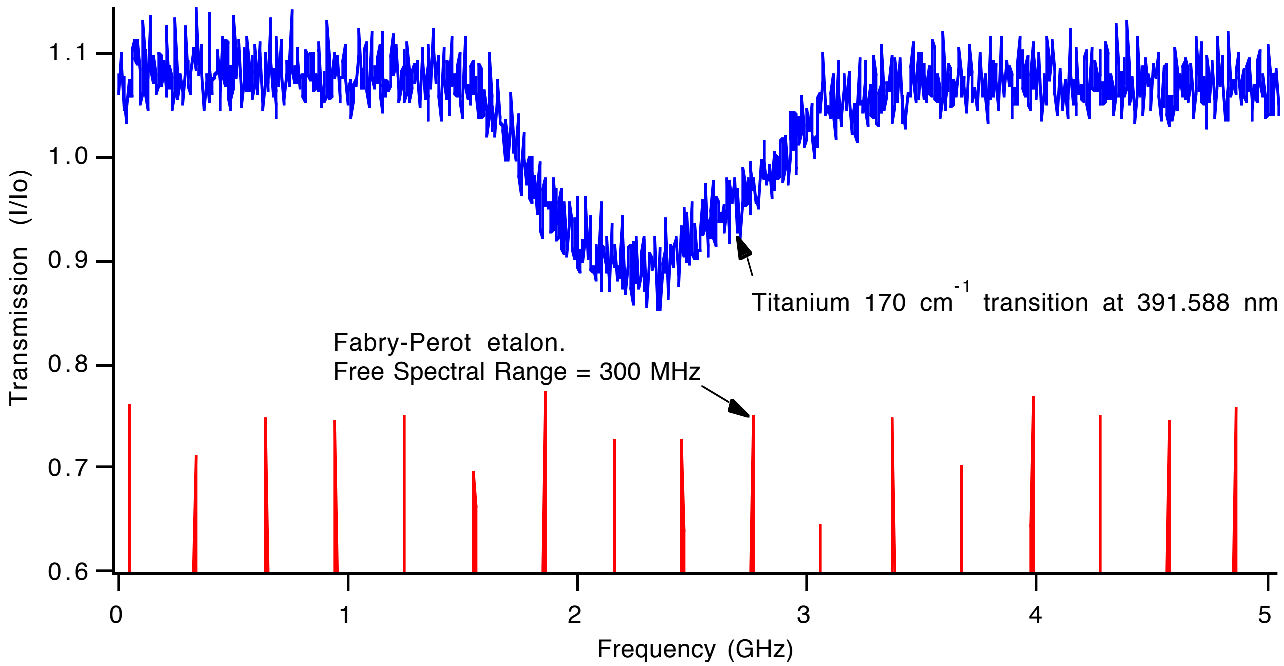

Figure 4.
Typical ground state Titanium vapor absorption line at 391 nm

For the group velocity delay technique, monitoring the phase delay induced by the vapor plume allows calculation of the transition density via equation 3.

$$\Delta\phi_{(\nu)} = \frac{\pi}{2} r_0 \, c \, \eta \, f \, \ell \left\{ g''(\nu) - g''(\nu - \nu_B) \right\} \tag{3}$$

where ν is the frequency offset of the laser from line center, $\Delta\phi(\nu)$ is the frequency dependent phase shift, r_0 is the classical electron radius, c is the speed of light, η is the density in the state being measured, f is the oscillator strength, ℓ is the path length through the vapor, g" is the imaginary portion of the complex line shape function (a Voight profile is typically used), and ν_B is the beat frequency.[6] At frequency offsets significantly larger than the Doppler or Lorentzian line widths, equation 3 can be simplified to equation 4.

$$Density \quad \eta = \frac{-2\Delta\phi(\nu - \nu_0)^2}{f \ell r_0 c \nu_B} \tag{4}$$

$$where$$

$$\nu_0 = frequency\ of\ atomic\ transition\ being\ used$$

Using equation 4, we can see that vapor density, is proportional to the phase shift $\Delta\phi$ and is proportional to the square of the frequency offset from the atomic transition. This means that for a large frequency offset, density is directly proportional to the group velocity delay induced by the vapor.

To measure the group velocity delay, we generate a probe beam that comprises two frequency components separated by a fixed frequency (200 MHz) and tune the laser through an optical transition in the vapor (see Figure 7). The group velocity delay technique is based on the measurement of the phase difference between two detector signals. Since silicon detectors cannot directly measure the phase of a laser beam, a laser beam is frequency-shifted by an acousto-optic modulator (Bragg cell) and then combined with the fundamental laser beam to create a beat signal (200 MHz) that can easily be detected and amplified. Using fast detectors with bandpass filters and ac-coupled amplifiers, we detect the optical beat frequency between the frequency components of the probe beam. We then propagate the probe beam through the vapor and measure its phase with respect to a reference beam using a vector voltmeter. Vapor-dependent phase changes can be resolved as low as about 4° (this corresponds to a group velocity delay of 56 ps for a 200 MHz beat signal). Velocity delay resolution can be increased, by increasing the optical beat frequency if necessary.

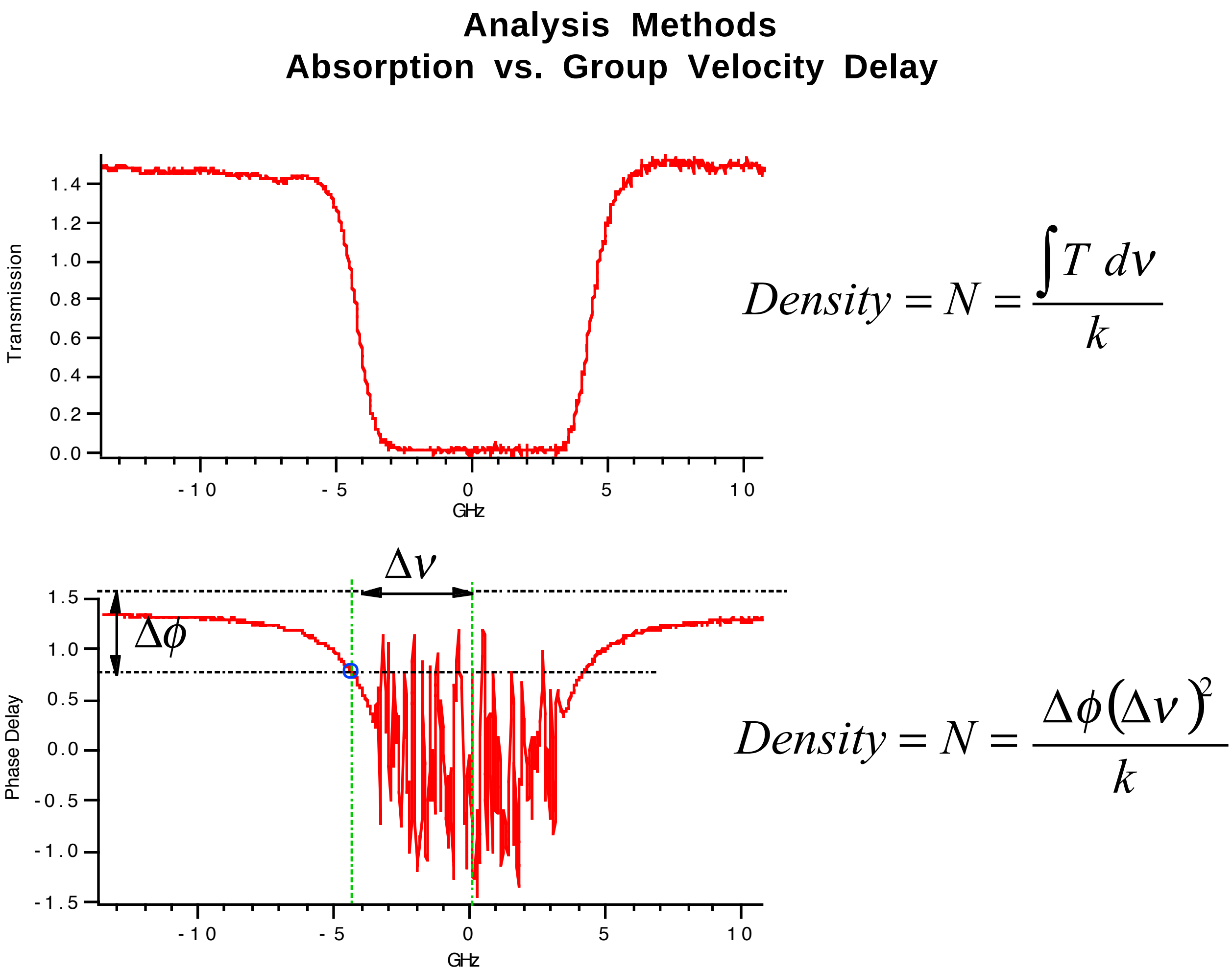

Figure 5.

Analysis methods: Laser Absorption Spectroscopy vs. Group Velocity Delay Spectroscopy

A direct comparison of GVDS and LAS analysis methods is shown in Figure 5. The top graph shows an very dense saturated atomic absorption line. Note that the line center of the atomic transition is completely saturated. In this region, the vapor plume becomes opaque to the probe laser. No useful absorption data exists in this area. The vapor density is beyond the dynamic range limit of the LAS analysis method and therefore cannot be readily measured. The bottom graph, shows the same transition recorded using the group velocity delay spectroscopy technique. The top horizontal dotted line on this graph is the baseline (no-vapor) group velocity delay. The second horizontal line is the group velocity delay of the vapor plume at the given offset frequency, $\Delta\nu$, where meaningful information is available.[7] By varying the offset of the laser from line center, we can extend the measurement range to vapor densities much larger than can be measured by LAS.

Another example of the extremely high dynamic range of the GVDS density monitoring technique is shown in Figure 6. The graphs show aluminum atomic vapor at the 394 nm ground state transition at two vapor density settings. The LAS and GVDS analysis methods are compared at low and high vapor densities. The three peaks visible in the low absorption graphs are aluminum hyperfine spectral features.

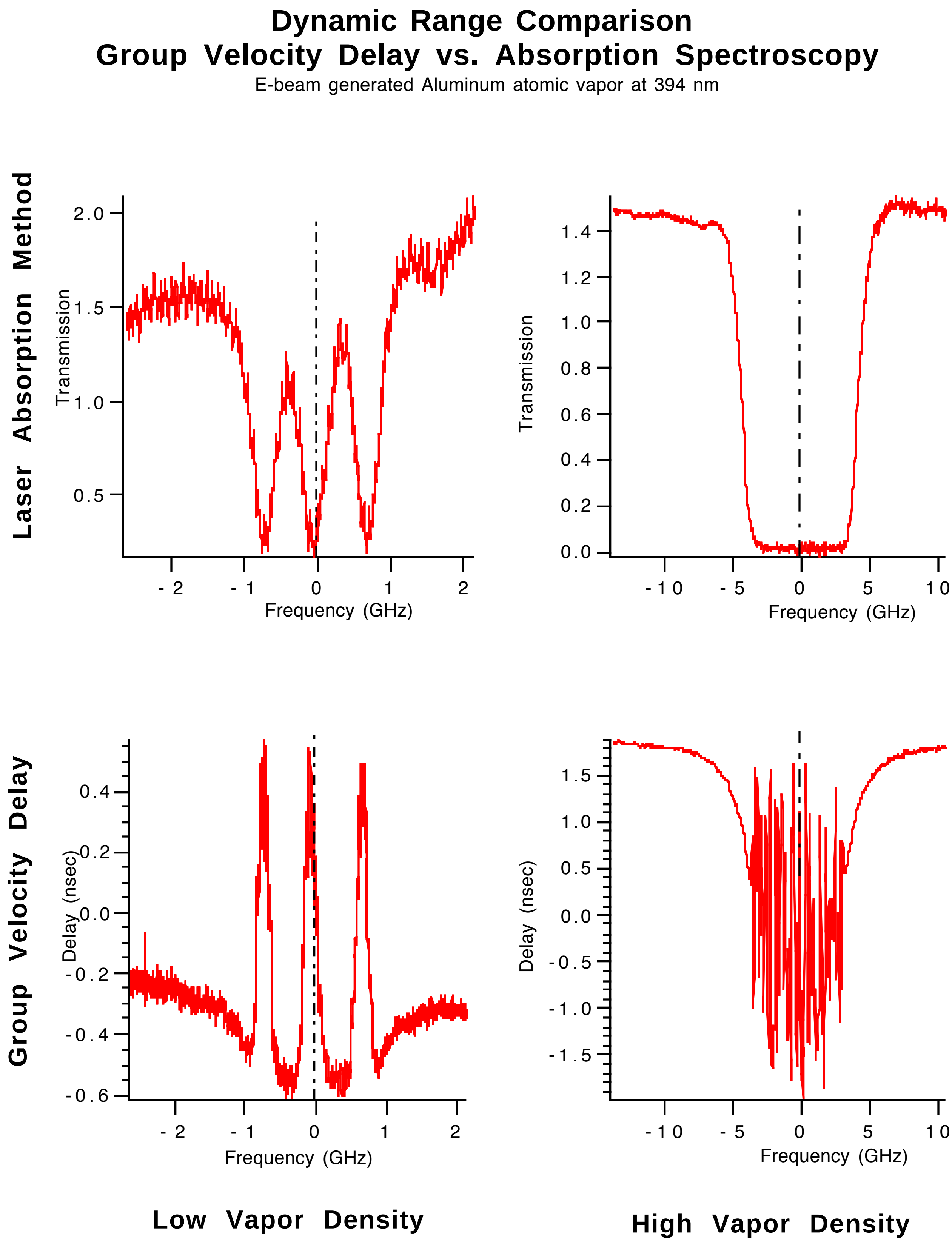

Figure 6.

Comparison between GVDS and LAS at low vapor density vs. high vapor density

Because the GVDS method is insensitive to line width, it possible to monitor extremely high vapor densities by moving the laser offset frequency farther from the saturated transition.

The optical layout of a typical GVDS density monitor is shown in Figure 7 below. A single mode external cavity diode laser (ECDL) is the laser source. For the GVDS sensor, the laser beam propagates through a Bragg cell where the beam is frequency-shifted 200 MHz. The original beam and the frequency-shifted beam are re-combined at the beamsplitter resulting in two beams each comprising two frequency components. When the beams reach the fast detectors, the optical beat signal ν_B can be detected. (Note there is also a standard LAS monitor included to produce LAS density measurements simultaneously with GVDS measurements.)

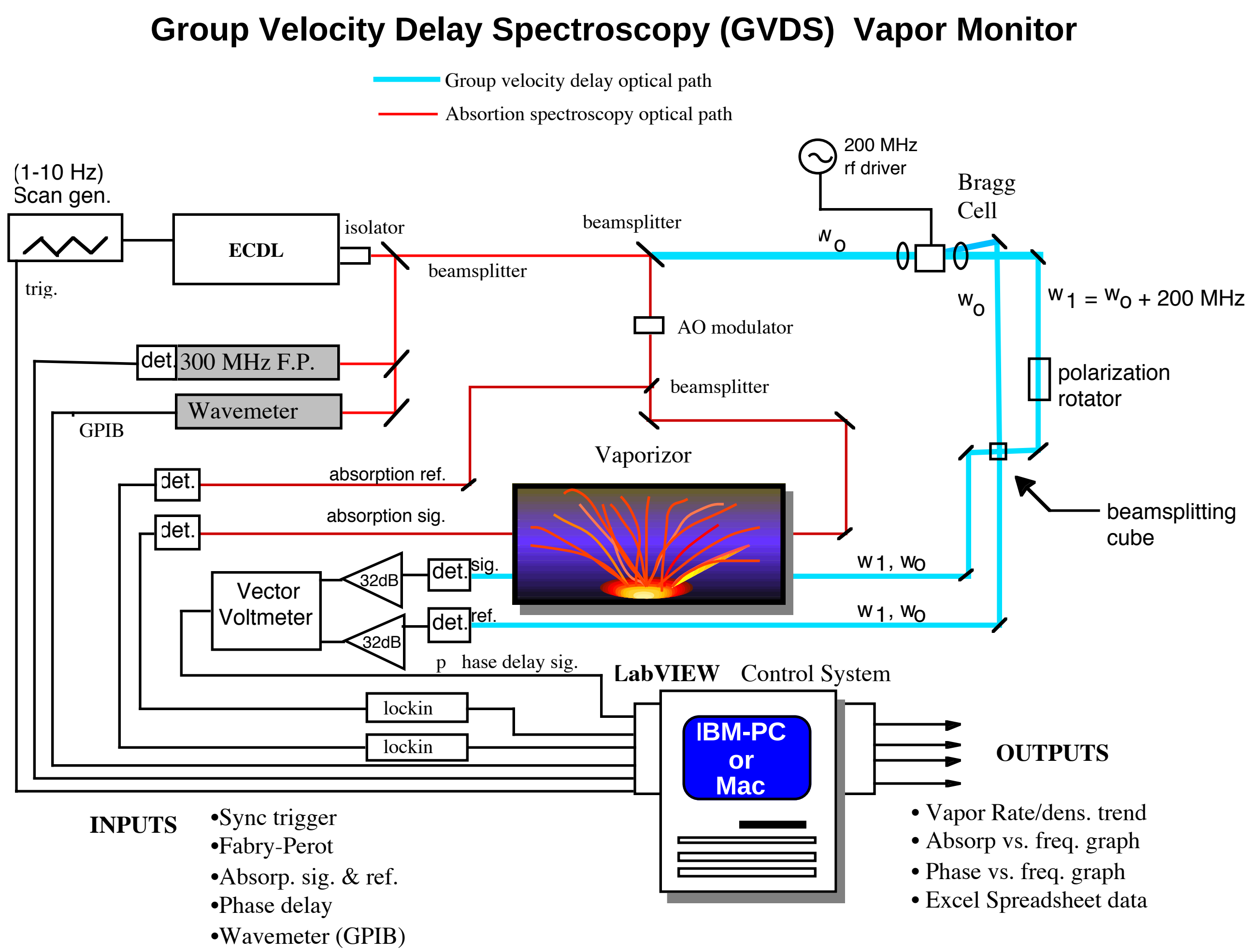

Figure 7.

Group Velocity Delay Spectroscopy (GVDS) Vapor Density Monitor

A LabVIEW program controls the acquisition of data. Group velocity delay information is acquired in the form of frequency scan waveforms for both LAS and GVDS methods. The program then analyzes each waveform and calculates the vapor density. Using a model based on process parameters, a vapor rate is calculated. The vapor rate is provided to the e-beam gun controller via an analog voltage. Work at the Lawrence Livermore National Laboratory is continuing on the development of GVDS vapor density monitors and controllers for aluminum and copper vapors.

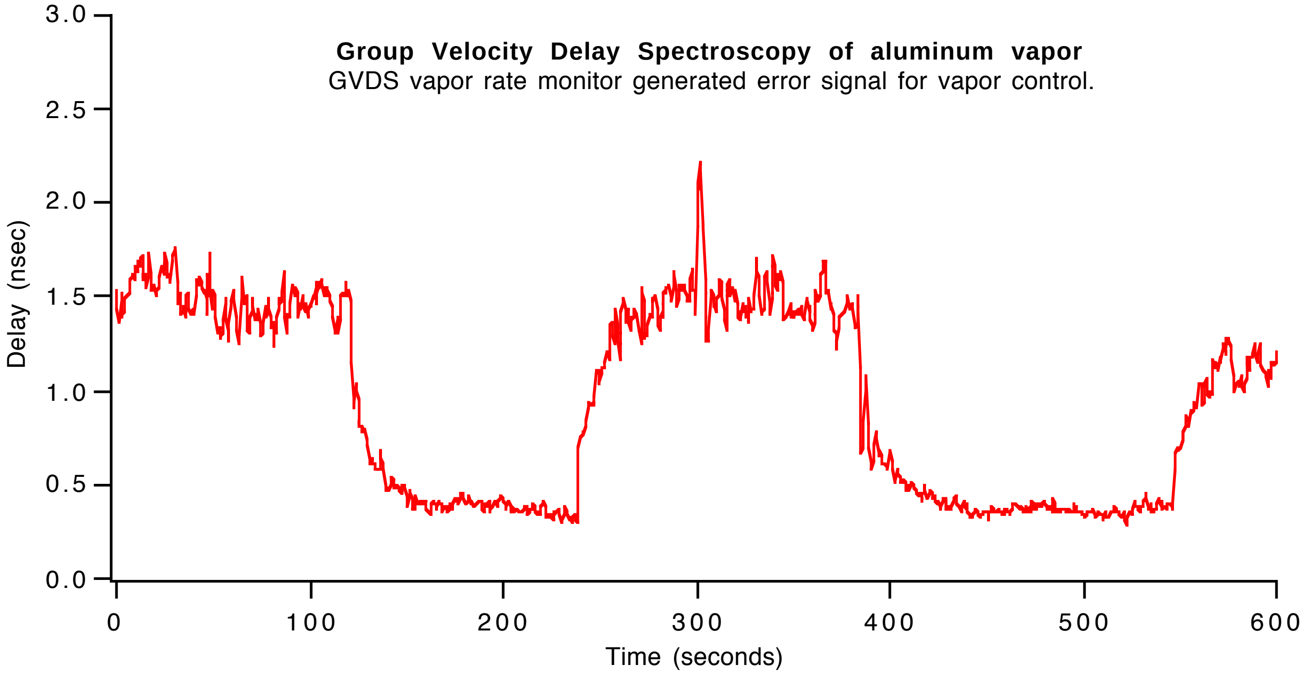

Figure 8.

GVDS process control of aluminum vapor rate demonstrated

Figure 8 shows data recorded at LLNL while controlling the aluminum vapor rate using the GVDS method. Note the aluminum vapor rate is held relatively constant between setpoint changes. The vapor density was changed by adjusting the process control setpoint on the e-beam current controller. Active control and stabilization of the vapor density was provided by a GVDS vapor density error signal sent to e-beam current controller. (The large spike in the center of the diagram was caused by an momentary arc in the e-beam gun.)

6. FUTURE DIRECTIONS

In parallel with the above efforts we are developing a copper vapor GVDS diagnostic for use in the production of yttrium-barium-copper-oxide (YBCO) high temperature superconductors. Electron beam PVD is actively being pursued as a path to high volume production. Critical to achieving success is accurate composition control of the deposited films. Yttrium and barium absorption monitors are straightforward because both have useful transitions that map well to available diode laser technology. Copper monitoring is more problematic. The longest wavelength transitions for monitoring the copper ground state are near 325 nm. Commercial systems have not been available for generating laser light at 325 nm that are suitable for industrial process control systems. We are working with an external cavity doubler manufactured by Laser Analytical Systems, Inc. as a route to a viable laser source for process monitoring in the blue and ultraviolet. Initial results at Laser Analytical Systems, Inc. indicate that pumping their external cavity with an external cavity diode laser is a viable approach at some wavelengths. The copper transitions at 325 nm are also too strong to use straight absorption spectroscopy to monitor the density. Copper in this application is therefore an ideal testbed for demonstrating the group velocity delay technique. We are working to demonstrate performance at 325 nm that is consistent with the group velocity delay technique. Combining these technologies will allow us to monitor copper vaporization with a robust sensor.

Both laser absorption spectroscopy (LAS) and group velocity delay spectroscopy (GVDS) are useful tools for monitoring electron beam generated vapor plumes. While LAS is well established and has been successfully deployed at several industrial sites, the atomic transition chosen to monitor the process must be carefully selected to match the process and process geometry. GVDS, while still in its infancy, offers the promise of a more generally applicable diagnostic. The large potential dynamic range accessible with this diagnostic would make it more process insensitive. It is ultimately a more complicated diagnostic requiring more sophisticated hardware and software to make accurate measurements. In order for GVDS to come into more common usage, the diagnostic set-up must be hardened for use in an industrial environment.

Replacing discrete components with fiber optic equivalents will help make the system more robust. At the same time careful optimization of the optical power must be performed. At present the group velocity delay technique requires significantly more optical power than laser absorption spectroscopy for the same signal to noise. The power required to produce adequate signal to noise can put prohibitive requirements on the laser system. This problem can be managed by more efficiently use of the light on the sending side as well as improvements in the process electronics on the receiving side. We plan on examining several options for both. In particular more direct ways of monitoring the phase difference between the signal and reference leg should both improve the realized accuracy and dynamic range as well as improve the optical power utilization.

Once these improvements are in place, it will be interesting to verify the actual range and accuracy of the diagnostic. While the present set-up is capable of measuring densities over a range of 10^3, improvements in the minimum detectable phase, minimizing phase noise, and improved analysis algorithms should yield several more orders of magnitude in dynamic range. This test will be key to demonstrating whether the GVDS technique has the broad applicability necessary for commercialization.

7. ACKNOWLEDGMENTS

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